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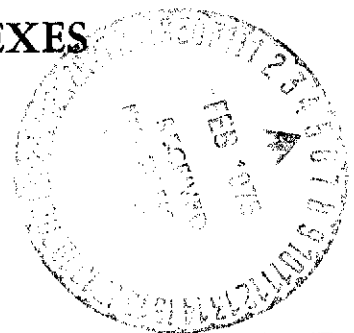
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**CONDUCTIVITIES OF THE IONIC COMPLEXES  
OF TWO CYCLIC POLYETHERS**

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# CONDUCTIVITIES OF THE IONIC COMPLEXES OF TWO CYCLIC POLYETHERS

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## SUMMARY

The conductivities of the solid potassium thiocyanate complex of both dicyclohexyl-18-crown-6 and dibenzo-18-crown-6 were measured at 300 K (27° C). Saturated aqueous potassium thiocyanate and graphite were used as ion-transporting and ion-blocking electrodes, respectively. The ionic conductivity predominated for both samples, but it was many orders of magnitude smaller than the value previously reported. The ionic conductivity of the dicyclohexyl complex (the better conductor) was  $3 \times 10^{-6}$  per ohm-centimeter. Crown complexes, in general, do not appear promising as potassium ion solid electrolytes contrary to claims in the patent literature.

## INTRODUCTION

The dibenzo-18-crown-6 and the dicyclohexyl-18-crown-6 belong to a class of compounds known as macrocyclic polyethers which are commonly called crown compounds. Their discovery in 1967 (ref. 1) opened a new door because these are the only neutral synthetic compounds to form stable complexes both in solution and in the crystalline form with salts of alkali metals. The structures of the macrocyclic polyethers are similar to those of certain naturally occurring macrocyclic antibiotics, such as valinomycin and nonactin, which influence the transport of sodium and potassium ions across cell membranes. Several articles which discuss the macrocyclic polyethers and their complexes also give detailed synthesis information (refs. 2 to 4). A recent patent (ref. 5) reported that the solid potassium thiocyanate complex of the dicyclohexyl and also of the dibenzo-18-crown-6 may be potassium ion conductors with exceedingly high conductivity. For example, values of from 0.7 to 1.3 per ohm-centimeter at room temperature were cited for the dicyclohexyl complex.

Solid ionic conductors, which have reasonably large alkali ion conductivities, are of interest as solid electrolytes for high energy density battery systems. For example,

sodium beta-alumina, a sodium ion conductor, with a conductivity of about 0.2 per ohm-centimeter at 573 K (300° C) is being used to develop a sodium/sulfur secondary battery (ref. 6). As the patent (ref. 5) points out, materials with alkali ion conductivities of this order or larger at room temperature would be of considerable interest for an improved high energy battery technology based on potassium negative electrodes. To explore these possibilities, conductivity measurements were made on the solid potassium thiocyanate complex of both the dicyclohexyl and dibenzo crown compounds. The results are compared with those reported in the patent.

## EXPERIMENTAL

The white crystalline complexes used for this study were synthesized at E. I. DuPont de Nemours Co. They were the potassium thiocyanate complex of both the dicyclohexyl and dibenzo-18-crown-6 compounds.

A sample of each complex was made into a disk (about 1.2 cm diam and 0.3 cm thickness) by pressing at  $1.4 \times 10^8$  newtons per square meter (20 000 psi) for several hours. Following this the disks were still relatively porous and fragile. To prevent electrical shorting by seepage of the liquid electrodes through the disk, the pores were filled with a polystyrene polymer following the procedure developed by Mitoff (ref. 7). After the polymer hardened, the faces of both disks were sanded with fine carborundum paper to remove any surface blocking layer of polymer insuring electrolyte-electrode contact.

Both ionic and electronic conductivity measurements were made. For the ionic conductivities, reversible electrodes of an aqueous saturated solution of potassium thiocyanate (KCNS) were used. The apparatus is shown in figure 1. The platinum lead wires, while close to the disk to minimize electrode resistance, were not allowed to contact the disk. This permitted measurements of the ionic conductivity but blocked the electronic conductivity. For the electronic conductivity measurements, ion-blocking measurements were made similar to the Wagner method (ref. 8). A graphite electrode (an emulsion of colloidal graphite in isopropyl alcohol) was applied to one face and solid potassium to the other. Contact between the sample and the potassium was maintained by moderate spring tension. Platinum foil and wire were used for the electrical leads.

The direct current conductivities of both disks were measured at 300 K (27° C). A constant potential of about 1.54 volts was applied, and the corresponding potentials across the sample and a standard resistor ( $10^6$  ohms), in series with the sample, were measured with time by either an oscilloscope or an electrometer. The direct current conductivities were then calculated. For comparison, an alternating current conductivity for the dicyclohexyl crown complex, using the potassium thiocyanate solution contacts, was obtained at  $10^3$  hertz using an impedance comparator bridge and standard resistors.

## RESULTS AND DISCUSSION

The conductivity results for both samples are shown in figure 2. The direct current conductivities for the dicyclohexyl and the dibenzo complexes are shown as solid and dashed lines, respectively. The alternating current conductivity for the dicyclohexyl complex at  $10^3$  hertz (shown in fig. 2) was in good agreement with the corresponding direct current conductivity.

The ionic conductivities predominated for both samples, as suggested by a comparison of the results obtained using electrodes of potassium thiocyanate solution and graphite. For example, after 1 second, the ionic conductivities of the complex of the dibenzo-18-crown-6 and the dicyclohexyl-18-crown-6 were of the order of 10 and  $10^3$  larger than their respective electronic conductivities. The ionic conductivity of the dicyclohexyl complex was reasonably constant up to about 1 second but then decreased somewhat - presumably due to polarization of the potassium thiocyanate electrodes.

However, the ionic conductivities for both complexes were still several orders of magnitude smaller than that value of 1 per ohm-centimeter reported in the patent (ref. 5). For example, the ionic conductivity of the dicyclohexyl complex, the better conductor, was only about  $3 \times 10^{-6}$  per ohm-centimeter at 300 K ( $27^\circ$  C). One possible explanation for this apparent significant difference in conductivities is that the sample used in the referenced work may have had a crack or a flaw which resulted in the higher conductivities.

Because of the very low conductivities obtained for the dicyclohexyl and dibenzo potassium thiocyanate complexes, crown complexes, in general, are not promising as solid electrolytes for high energy density battery systems even in thin film configurations.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, December 16, 1974,  
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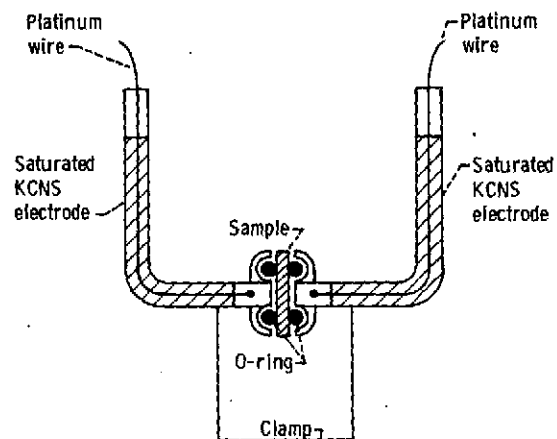


Figure 1. - Conductivity cell.

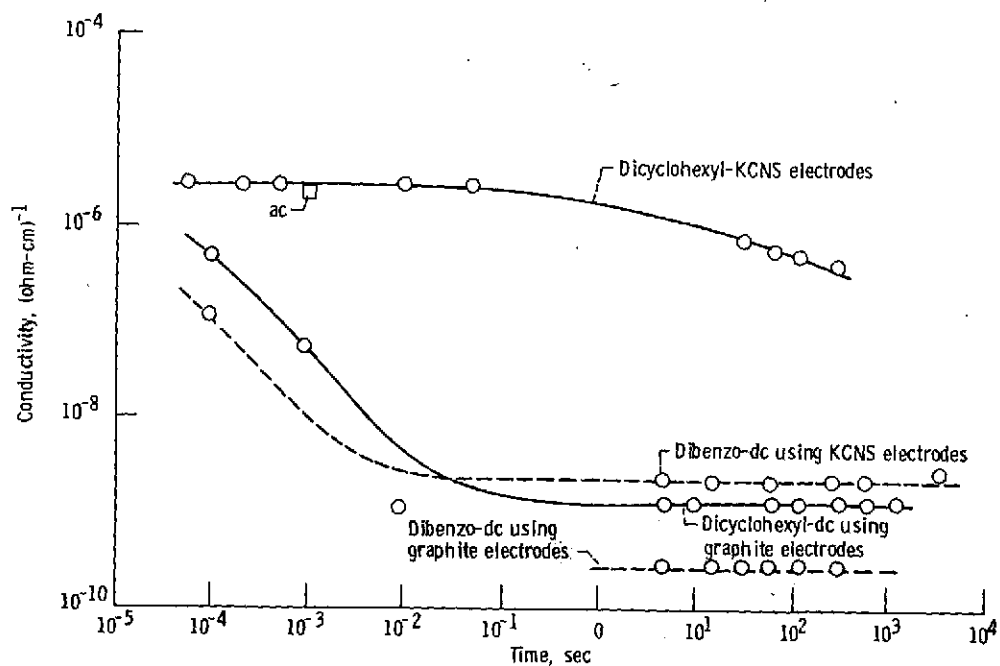


Figure 2. - Conductivity of dicyclohexyl and Dibenzo Crown-KCNS complexes at 300 K.